

Japanese Kokoku Patent No. Sho 44[1969]-21559



JP

44-21559

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SEP 11 2000  
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Code: 778-78340  
Ref. No.: CM-006 NEH

JAPANESE PATENT OFFICE  
PATENT JOURNAL  
KOKOKU PATENT NO. SHO 44[1969]-21559

Japanese Cl.: 24 F 0  
26 E 0  
25 D 0  
25 H 371

Filing No.: Sho 40[1965]-66491

Filing Date: October 28, 1965

Publication Date: September 13, 1969

No. of Inventions: 1 (Total of 5 pages)

COATING COMPOSITION FOR RUBBER

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[There are no amendments to this patent.]

Detailed explanation of the invention

The present invention pertains to a coating composition for rubber, wherein the product of esterification of a synthetic rubber or natural rubber containing a carboxyl group and a polyester or polyether having an hydroxyl group is used as a coating vehicle for rubber; sulfur, vulcanization accelerators, pigments, etc., are added and the composition is diluted with a solvent, and [the composition] is capable of firmly bonding with rubber as a result of curing based on crosslinking with the rubber molecules.

In the past, oil-based paints were commonly used for coating rubber, and in recent years, synthetic resin coating materials have been used in some cases.

Synthetic resin coating materials exhibit good weather resistance, oil resistance, and chemical resistance, but the crucial deficiency in the above-mentioned materials is insufficient adhesion: thus, many restrictions are placed on applications. Furthermore, flexibility and elasticity of coating compositions for rubber are required; thus, a plasticizer is mixed to impart flexibility.

In this case, the plasticizer migrates toward the rubber during the course of application, and as a result, the coated film becomes hardened during application and formation of cracks and delamination frequently occur. Furthermore, because the plasticizer in the coating migrates to the surface of the rubber, adhesion is reduced. The above-mentioned defect in conventional coating compositions for rubber is caused by the fact that the adhesion with rubber is simply based on secondary adhesion resulting from cohesive forces alone, and mechanical properties such as flexibility, elasticity, and abrasion resistance of the coated film are not sufficient. Thus, a coating material capable of achieving an adequate result when used for rubber products subjected to repeated torsional forces such as bending, stretching, and compression does not exist.

In the present invention, problems of the above-mentioned coating composition for rubber are improved, and the purpose of the present invention is to produce a coating composition for rubber having excellent properties such as high elasticity, flexibility, abrasion resistance, and weather resistance and which is capable of undergoing curing with sulfur and forming a high adhesion based on crosslinking with the vulcanized rubber molecules and firm chemical bonding.

The coating composition for rubber of the present invention is a coating composition wherein the product of an esterification reaction of a synthetic rubber or natural rubber

containing a carboxyl group and a polyester or polyether having a hydroxyl group is used as a vehicle, and the rubber coating composition is produced by adding appropriate amounts of sulfur, vulcanization accelerators, pigments, etc.

For the synthetic rubber having a carboxyl group used in the present invention, synthetic rubber produced by copolymerization reaction of a monomer having a carboxyl group such as butadiene-methacrylic acid copolymer, butadiene-acrylonitrile-methacrylic acid terpolymer, and butadiene-styrene-methacrylic acid terpolymer as one component, can be mentioned.

Furthermore, for the carboxylic acid derivative of natural rubber or synthetic rubber used in the present invention, a material produced by modification of a rubber-like polymer having a double bond such as natural rubber, polyisoprene rubber, polybutadiene rubber, polychloroprene rubber, and butadiene-styrene copolymer rubber with an organic compound having a carboxyl group and capable of addition with a substance having a double bond such as maleic anhydride, itaconic acid, or thioglycolic acid can be mentioned.

As a method used for production of the carboxylic acid derivative from a rubbery polymer having a double bond, for example, a so-called mechanochemical method wherein thorough mixing is provided for the rubbery polymer and a reagent used for induction of the carboxyl group used in the oxidation modification reaction on a standard rubber processing roll, can be mentioned. In this case, it is desirable when shearing of the rubber molecules is done as much as possible using one of the following methods, for example, thorough mixing of the rubber is carried out before oxidation, roll mixing is provided for a sufficient time to initiate the oxidation reaction, or roll mixing is provided in the presence of an appropriate [illegible] agent. The reason is that the molecular weight of standard rubbery polymers is very high, and the viscosity of the solution produced by dissolving such polymers in an organic solvent is high and handling is difficult; furthermore, the coating operation is difficult when the solution is used for coating. Based on the above background, the best method for production of the carboxylic acid derivative of a natural rubber or synthetic rubber in the present invention is the method described below. That is, a method for production of a carboxylic acid derivative of a natural rubber or synthetic rubber wherein a radical initiator such as a peroxide or azo compound is added to the organic solvent solution of a natural rubber or synthetic rubber and kneaded ahead of time, stirring is provided in air under heat to sufficiently reduce the viscosity of the above-mentioned solution; then, the reagent used for induction of a carboxyl group, such as thioglycolic acid, maleic anhydride, or itaconic acid is added and further stirring is provided under heat.

For polyethers and polyesters having a hydroxyl group used for modification by means of esterification of a synthetic rubber having a carboxyl group, or a rubbery polymer having a carboxyl group such as a carboxylic acid derivative of a natural rubber or synthetic rubber, those having one hydroxyl group in the molecule are especially desirable, but those having two or more

hydroxyl groups can be used as well. However, when a polyester or polyether having at least two different hydroxyl groups in a single molecule is used, and when a polyether or polyester containing a hydroxyl group with an amount less than that which will react with the carboxyl group included in the rubbery polymer, crosslinking reaction is likely to occur during the esterification reaction and gelation of the rubbery polymer solution is likely to occur; thus, when esterification is carried out for a rubbery polymer containing a carboxyl group, an excess of hydroxyl group is required.

For the polyether used in the present invention, for example, a polyoxyalkylene compound having a hydroxyl group with a molecular weight of 4000 or below produced by a ring-opening polymerization reaction carried out for a material such as ethylene oxide, propylene oxide, butylene oxide or tetrahydrofuran can be mentioned.

Furthermore, for the polyester used in the present invention, a polymer produced by a ring-opening polymerization reaction carried out for a lactone, or a polymer with a molecular weight of 4000 or below produced by polycondensation of a dibasic acid and diol can be mentioned. In this case, for examples of dibasic acids, saturated fatty acids such as oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid and isosebacic acid, unsaturated fatty acids such as maleic acid and fumaric acid, and aromatic carboxylic acids such as phthalic acid and isophthalic acid, etc., can be mentioned. Furthermore, as examples of diols, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, butylene glycol, allyloxypropanediol, trimethylolpropane monoallyl ether, etc., can be mentioned.

The reason the molecular weight of the polyether or polyester is limited to 4000 or less is because the solution viscosity becomes too high and the modified material cannot be used as a coating material when esterification is carried out for a rubbery polymer having a carboxyl group using a material with a molecular weight greater than 4000.

As for the method used for modification based on esterification of a rubbery polymer containing a carboxyl group, standard esterification methods commonly used can be used in this case as well. For example, the reaction progresses quantitatively when a method is used wherein stirring is provided for an organic solvent under heat at a temperature of 160-230°C in the presence of an esterification reaction catalyst, while continuously removing the water generated.

The rubbery polymer containing a carboxyl group modified with a polyether or polyester produced as described above can be used effectively as a vehicle for the coating material. For example, in addition to the features of standard carboxyl rubbers such as high solvent resistance and good apparent drying property of the coating material, improved flexibility and weather resistance based on the polyether or polyester, as well as increased tear strength can be achieved.

As described above, the coating composition for rubber of the present invention is produced by dissolving the above-mentioned vehicle and sulfur, vulcanization accelerators, pigments, etc., in a solvent.

When the above-mentioned coating material is coated onto the surface of a vulcanized rubber, for example, and baking is carried out at 100-160°C for 2-20 min, coating can be achieved. Furthermore, when coating is done for the surface of a nonvulcanized rubber, curing and hardening can be achieved during the course of vulcanization of the rubber.

The coating composition for rubber of the present invention bonds with the coating object rubber surface with complete chemical bonding based on sulfur; thus, a very high adhesive strength can be achieved on the surface of a rubber subjected to repeated bending, stretching, compression, etc., and a coated film with very high elasticity, flexibility, abrasion resistance, weather resistance, etc., can be produced.

In the following, the present invention is explained further in specific terms with application examples, but the invention is not limited to these examples.

#### Application Example 1

##### i) Production of a carboxylic acid derivative of natural rubber

When 3 wt% azobisisobutyronitrile is added to the rubber component in a 10% xylylol solution of a natural rubber, and stirring is provided under heat at a temperature of 80°C for 24 h while bubbling air, the viscosity is reduced from an initial 2000 cps to 70 cps. For 300 g of the above-mentioned xylylol solution of a natural rubber (natural rubber component of 30 g), 1 g thioglycolic acid is added, and when stirring is provided for 3 h under heat at a temperature of 120°C, a natural rubber-thioglycolic acid adduct can be produced.

##### ii) Synthesis of polyester

106 g (1 mol) diethylene glycol, 132 g (1 mol) allyloxypropanediol, 102 g (0.7 mol) adipic acid, 148 g (1 mol) phthalic anhydride, and 4 g tetrabutyl titanate as a catalyst, and 30 g of mixed xylene as a solvent were poured into a reaction flask and stirring was provided under heat at a temperature of 160-230°C for 6 h. Furthermore, an azeotropic reaction was carried out for the water generated with xylene and [the water was] continuously removed from the system. In this manner, a polyester with an acid value of 1.63, hydroxyl group value of 36.1, and viscosity of 2300 cps was produced at 25°C.

##### iii) Polyester-modification reaction for natural rubber-thioglycolic acid adduct

300 g of the 10% xylylol solution of a natural rubber (rubber component of 30 g) produced in i) above, 33.6 g polyester produced in ii) above, and 1 g p-toluenesulfonic acid as a catalyst were poured into a reaction flask and stirring was provided in the presence of a nitrogen gas for 1 h under heat at a temperature of 140-150°C and for 8 h under heat at a temperature of

160-230°C. In this case, an azeotropic reaction was carried out with xylylol for the water generated (0.2cc) and continuously removed outside the system. In this manner, a rubber coating vehicle is produced.

Furthermore, in the above-mentioned application example, a reaction was carried out for 1 Eq of carboxyl group in the modified rubber and 2 Eq of hydroxyl group in the polyester.

iv) Production of coating material

Mixing is carried out for the vehicle produced in iii) above as shown below and production of a rubber coating material is carried out.

	Parts by weight
Vehicle	200
(xylylol solution with a solid component of 50%)	
Sulfur	4
Rutile type titanium oxide	50
Zinc white P	4
(light calcium carbonate treated with stearic acid)	
Vulcanization accelerator M	8
(Mercaptobenzothiazole)	
Vulcanization accelerator PZ	2
(Zinc dimethyldithiocarbamate)	
Zinc oxide	8
Stearic acid	0.5
Cellosolve acetate	80
Ethyl acetate	40

A thorough kneading is performed for the above-mentioned composition by a paint roll to produce a coating material. Properties of the above-mentioned coating material vulcanized for 5 min at 140 °C are:

Tensile strength	103 kg/cm <sup>2</sup>
Elongation at break	350%

Furthermore, when the above-mentioned coating material was coated onto a vulcanized rubber with a hardness of 60° and vulcanization was carried out at 140°C for 5 min, very good adhesion between the coated film and the surface of the rubber was achieved and peeling with a knife was not possible, and no change was observed when a cross-cut adhesion test (a test method where lines are cut in the vertical direction and horizontal direction with a sharp knife at intervals of 1 mm and an adhesive tape is peeled) was performed, and no changes were observed

even after a 100,000-cycle bending test using the Demashar [transliteration] bending test (distortion of 30%).

Furthermore, the gloss of the coated film is good, weather resistance and oil resistance are very good, and when a test was carried out in a weatherometer for 50 h, discoloration was absent, and delamination was absent after dipping the film in 20°C toluene for 48 h.

### Application Example 2

300 g of the 10% xylylol solution of natural rubber (rubber component of 30 g) produced above in i) of Application Example 1, 100 g of the polyester produced above in ii) of Application Example 1, and 1 g p-toluenesulfonic acid as a catalyst were poured into a reaction flask and stirring was provided in the presence of nitrogen gas for 1 h under heat at a temperature of 140-150°C and for 8 h under heat at a temperature of 160-230°C. In this case, an azeotropic reaction was carried out for the water generated with xylene and water was continuously removed from the system.

In the above-mentioned application example, a very high proportion of hydroxyl groups (0.064 Eq) included in the polyester is used to the carboxyl groups included in the modified rubber (0.0108 Eq), but an allyl ether group based on the crosslinking reaction is included in the polyester used; thus, the properties of the coating material are not adversely effected even when an excess of polyester that has not been grafted to the rubber molecule remains.

Production of a rubber coating material with the vehicle produced as described above was done using the same composition described in iv) of Application Example 1.

Properties of the above-mentioned coating material vulcanized for 5 min at 140°C were:

Tensile strength	123 kg/cm <sup>2</sup>
Elongation at break	180%

Furthermore, when the above-mentioned coating material was coated onto a vulcanized rubber with a hardness of 60° and vulcanization was performed at 140°C for 5 min, very good adhesion between the coated film and the surface of the rubber was achieved and no changes were observed when the cross-cut adhesion test was performed, and no changes were observed even after a bending test of 100,000 cycles was carried out using a Demashar bending test (distortion of 30%). Furthermore, the gloss of the coated film is good, weather resistance and oil resistance are very good, and when a test was performed by a weatherometer for 50 h, discoloration was absent, and delamination was absent after dipping the film in 20°C toluene for 48 h.



### Application Example 3

3 wt% benzoyl peroxide was added to the rubber component of a 10% xylylol solution of natural rubber and stirring was performed under heat at a temperature of 80°C for 24 h as bubbling of air was performed. In this manner, a 10% xylylol solution of a natural rubber with a viscosity of 70 cps (20°C) was produced. 1.5 g maleic anhydride were added to 300 g of the above-mentioned solution and stirring was provided for 3 h under heat at a temperature of 120°C to produce a natural rubber-maleic anhydride adduct.

Furthermore, after the above-mentioned adduct reaction, washing of the above-mentioned reaction mixture was done with ethyl acetate and extraction of the nonreacting maleic anhydride was achieved, and when the acid value of the reaction product was measured, oxidation of 82% of the maleic anhydride to the natural rubber was obtained.

30 g of the above-mentioned natural rubber-maleic anhydride adduct, 120 g polyoxypropylene glycol (molecular weight 2000), 2 g tetrabutyl titanate used as a catalyst, and 50 g xylylol used as a solvent were poured into a reaction flask and stirring was provided under heat at a temperature of 160-230°C for 17 h in the presence of nitrogen gas. In this case, an azeotropic reaction was carried out for water generated with xylylol and [the water was] continuously removed from the system. Production of a rubber coating material was carried out with the rubber coating material vehicle produced as described above using the same composition described in Application Example 1.

Properties of the above-mentioned coating material vulcanized for 5 min at 140°C are:

Tensile strength                      150 kg/cm<sup>2</sup>

Elongation at break                  450%

Furthermore, when the above-mentioned coating material was coated onto a vulcanized rubber with a hardness of 60° and vulcanization was carried out at 140°C for 5 min, very good properties of the coated film were achieved. For example, the test results are as shown below.

Adhesion: cross-cut adhesion test:    No change

Weather resistance: Problems such as formation of cracks and discoloration were absent when an exposure test was performed by a weatherometer for 50 h. Furthermore, no change was observed at all after a 30-day outside sunlight exposure test.

Bending test: no change was observed even after a 100,000-cycle bending test using a Demashar bending test (distortion of 30%).

### Application Example 4

A thorough mixing was carried out for 100 g of a commercial carboxylated rubber, Hycar 1000 x 145 (a random copolymer of butadiene and acrylic acid, acid value 70) by a rubber roll, which was subsequently dissolved in 400 g xylylol. 3 g azobisisobutyronitrile were added to the

above-mentioned solution, [and] stirring was continued under heat at 80°C for 24 h as bubbling of air was performed.

Then, 133 g of a polyester glycol produced by performing a ring-opening polymerization reaction for an  $\epsilon$ -caprolactam were added to the above-mentioned rubber solution with a low viscosity, and stirring was performed for 18 h under heat at a temperature of 160-230°C in the presence of a nitrogen gas, and an esterification reaction was carried out. Furthermore, the above-mentioned polyester is produced by a ring-opening polymerization reaction using 1 mol of 1,4-butanediol to 8 mol  $\epsilon$ -caprolactam, and the acid value is 0.22, hydroxyl group value is 105.7 and the molecular weight is 1062.

In this case, an azeotropic reaction was performed for the water generated (2.1 cc) with xylyl and [the water was] continuously removed from the system.

Production of a rubber coating material was carried out with the rubber coating vehicle produced above with the composition shown below.

	Parts by weight
Vehicle	100
(without a solvent, solid component of 100%)	
Sulfur	4
Zinc oxide	5
Stearic acid	0.2
Accelerator M	5
(mercaptobenzothiazole)	
Accelerator TT	0.2
(tetramethylthiuram disulfide)	
Toluol	40
Xylol	60
Carbon tetrachloride	100

Properties of the above-mentioned coating material vulcanized for 10 min at 140°C were:

Tensile strength            130 kg/cm<sup>2</sup>

Elongation at break        450%

Furthermore, when the above-mentioned coating material was coated onto a vulcanized rubber, very good flexibility, adhesion, weather resistance, etc., was achieved.

Claims

A coating composition for rubbers, wherein the esterification reaction product of a synthetic rubber or natural rubber containing a carboxyl group and a polyester or polyether having a hydroxyl group is used as a vehicle, and sulfur, vulcanization accelerators, pigments, etc., are added to the composition.